

# Ethylenediamine attached to silica as an efficient, reusable nanocatalyst for the addition of nitromethane to cyclopentenone

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## Abstract

A solid base nanocatalyst was obtained by co-condensation between tetraethylorthosilicate (TEOS) and 3-glycidoxypropyltrimethoxysilane around a neutral *n*-dodecylamine template. The glycidoxy ring was opened by reaction with ethylenediamine, to give the desired Caten nanocatalyst. Thermogravimetric analysis showed that the number of active basic groups in this nanocatalyst is  $1.22 \text{ mmol g}^{-1}$ . Its TEM image showed that its individual particle is spherical, with a size of approximately 50 nm. Nitrogen adsorption–desorption isotherms gave evidence that this nanocatalyst has a mesoporous structure with pore diameter and surface area of 5.2 nm and  $796.1 \text{ m}^2 \text{ g}^{-1}$ , respectively. Analyses by  $^{13}\text{C}$  and  $^{29}\text{Si}$  nuclei NMR confirmed the obtention of the catalyst proposed in the synthetic route. The obtained material was used as catalyst in the addition of nitromethane to cyclopentenone in equimolar amounts, and yields of nitromethylcyclopentanone as high as 98% were achieved after only 30 min of reaction. It was possible to recover the catalyst from the reaction medium and recycle it 10 times.

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**Keywords:** Nanocatalyst; Michael addition; Silica

## 1. Introduction

In the last few years, literature has highlighted the importance of nanosized materials in several scientific and technological areas, and many research councils have intensified investments in nanotechnology for the coming years [1–7]. This motivation is based on the electronic, optical, electrooptical, electrochemical, and catalytic properties associated with colloidal particles of controlled nanosized materials. In this way, nanomaterials containing nanopores of uniform diameter and molecular dimensions may find potential use for the synthesis of organic compounds heterogeneous catalysis, as well as in the industrial production of chemicals [1–7].

Among several organic reactions, the Michael addition is a very important and versatile alternative for the obtention of carbon–carbon bonds, and nitro-compounds have been used in the conversion of these bonds into a variety of organic functional groups [8–13]. Because amine is a strong organic base [14], it has been used as catalyst for reactions such as Michael additions,

which involve carbon–carbon bond formation [15–17]. Therefore, the incorporation of basic organic groups into mesoporous silica has been described as an elegant method for the development of heterogeneous, reusable catalysts for Michael additions [18,19]. In this sense, nanosized catalysts, which have high surface area and lead to high product yields, have raised a lot of interest from researchers. These solid catalysts play a crucial role in product isolation and their reuse is easier if compared with homogeneous catalysts, features that make them a green alternative to the current homogeneous processes.

Therefore, the aim of this work is to report a new and simple method for the obtention of basic nanosilica by reaction of ethylenediamine with the pendant glycidoxy group of a previously modified silica. The catalytic activity of this novel material in the addition of nitromethane to cyclopentenone in equimolar conditions will also be reported here.

## 2. Experimental

### 2.1. Chemicals

The silica used in the formation of the inorganic framework was derived from tetraethylorthosilicate (TEOS) (Fluka).

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The silylant agent 3-glycidoxypropyltrimethoxysilane (Gly) (Sigma), ethylenediamine (en) (Acros), the surfactant *n*-dodecylamine (Sigma), xylene, and ethanol (Vetec) were all reagent grade.

## 2.2. Material preparation

The parent mesostructure was prepared by stirring *n*-dodecylamine (used as template, 0.55 g) suspended in water/ethanol (100.0 mL, 3:1, v/v) for 30 min. An opalescent solution resembling the nature of micelles was obtained. TEOS (2.76 mL) and Gly (0.57 mL) were added to this micellar suspension, and the mixture was stirred for 24 h. The template inside the pores of the synthesized compound was Soxhlet extracted with hot ethanol for 72 h, and the mesoporous hybrid, referred to as SiGly, was obtained as a solid material [20].

The resulting SiGly (5.00 g) was suspended in xylene (100.0 mL) and treated with ethylenediamine (6.8 mL) for 48 h, at reflux temperature. This was done in order to open the epoxy ring. The obtained solid was suspended in methanol and was cured in a hydrothermal system at 70 °C. The cured material was dried in vacuum at 100 °C to form the new basic nanomaterial which was, designated Caten.

## 2.3. Characterization

The amount of organic pendant chains co-condensed in the material Caten was determined by thermogravimetric analysis from the residual data, which was carried out by examining a Caten sample (approximately 10 mg) in a thermogravimetric analyzer, model TA-2960, under dynamic atmosphere consisting of dry nitrogen flux. Sample heating from room temperature up to 1000 °C was carried out at a heating rate of 10 °C min<sup>-1</sup>.

Scanning electron microscopy (SEM) was performed on a JEOL 840A. Samples were coated with carbon using a Balzer model MED 020 metalliser.

Nitrogen adsorption–desorption data were measured on a Quantachrome Nova 2200 analyzer, at 77 K. Surface area was calculated by the Brunauer–Emmett–Teller (BET) method, and pore size distribution was derived from the adsorption branches of the isotherms using the Barrett–Joyner–Halenda (BJH) method.

Infrared spectra of all the samples were performed in KBr pellets, in the 4000–400 cm<sup>-1</sup> region, with a resolution of 4 cm<sup>-1</sup>. To this end, 64 scans were accumulated, and spectra were recorded on an MB-100 Bomem FTIR spectrophotometer.

TEM analysis of the synthesized catalyst was carried out by means of a transmission electron microscope Jeol 100C operating at 80 kV. The sample was distributed on 200 mesh carbon coated copper grids.

<sup>29</sup>Si and <sup>13</sup>C nuclear magnetic resonance spectra of the solid sample were obtained on a Varian Mercury Plus 300 spectrometer, at room temperature. For each run, approximately 1 g of catalyst was compacted into a 7 mm silicon nitrite rotor. The measurements were obtained at 75.47 and 59.61 MHz, for carbon and silicon, respectively, with a magic-angle spinning speed of 3 kHz. In order to increase the signal-to-noise ratio of the

solid state spectra, the CP/MAS technique was used. <sup>29</sup>Si and <sup>13</sup>C CP/MAS spectra were obtained with pulse repetitions of 1 and 2 s and contact times of 1 and 4 ms, respectively.

## 2.4. Reaction of nitromethane with cyclopentenone catalyzed by the Caten nanocatalyst

The catalytic reactions were carried out by mixing cyclopentenone (0.06 mL, 0.6 mmol) and nitromethane (0.03 mL, 0.6 mmol) in equimolar conditions, in the presence of the Caten nanocatalyst (0.10 g), in ethanol (2.00 mL). The reaction mixture was stirred at 50 °C up to the termination of the reaction. The end of the reaction between nitromethane and cyclopentenone was determined by thin layer chromatography on silica gel using hexane/ethyl acetate (85:15, v/v) as eluent.

The catalyst was removed from the solution by filtration and the product was characterized by <sup>1</sup>H NMR at a frequency of 300 MHz, in CDCl<sub>3</sub>, on a Varian Mercury Plus 300 spectrometer, at room temperature. The amount of 3-nitromethylcyclopentanone produced in the reaction was determined on an HPLC system from Perkin-Elmer, Series 200, equipped with an LC Series 200 pump, a Series 200 UV–vis detector, and a Spheri-5 RP-18 column with partial size of 5 mm. Manual injection was carried out with a 20 mL loop, using water/methanol (60:40, v/v) as the mobile phase. All the analyses were done in triplicate.

## 2.5. Kinetic studies

The kinetic studies were carried out under the same conditions described above, and the reactions were analyzed after 2, 5, 10, 12, 15, 20, 30, and 50 min.

After each reaction, the Caten nanocatalyst was filtered off and washed with ethanol. It was then reused in a further reaction between nitromethane and cyclopentenone, in order to evaluate its activity in successive recyclings.

# 3. Results and discussion

## 3.1. Nanocatalyst obtention and characterization

The synthetic procedure was based on the co-condensation between glycidoxypropyltrimethoxysilane (Gly) and TEOS, which yielded the SiGly material as represented in Fig. 1A. The amine surfactant micelles guide the formation of the silanol groups around the polar head of the micelle. Outside each pore, the hydrolyzed silicon atoms form siloxane groups, resulting in a crosslinked framework. This molecular arrangement favors the tetraethoxysilane compound in the hydrolyzing process, together with the presence of the silylating agent and causes an inorganic polymeric backbone formation in an organized form around the micelles. With such organization the amine groups of the *n*-dodecylamine molecules are directed to the available silanol groups and the corresponding aminoalkylsilyl groups are maintained around the micelles. The high density of the silanol groups dispersed over the pores form a homogeneous

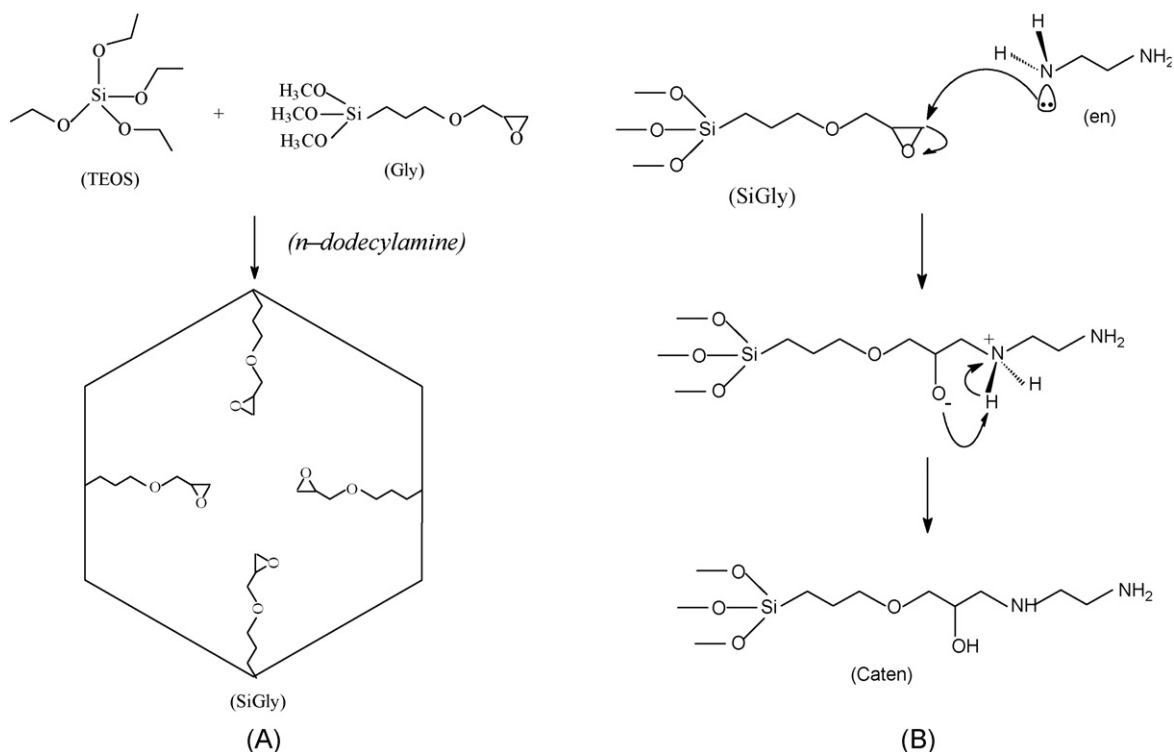


Fig. 1. Proposed mechanism for the co-condensation of TEOS and Gly around the micelle, to form the mesoporous silica SiGly (A); and proposed mechanism for the opening of the epoxy ring of SiGly by reaction with ethylenediamine, to give Caten nanocatalyst (B).

material. These structured silanol–surfactant interactions can be explained from electrostatic and hydrogen bond formation processes [21–23]. After template removal in refluxing ethanol the hexagonal mesoporous silica was isolated.

A typical nucleophilic attack of the basic nitrogen atom of ethylenediamine on the carbon atom of the ring produced the Caten nanocatalyst (Fig. 1B).

The organic group content was determined by TG analysis obtained from residual data (Fig. 2). This thermogravimetric curve shows a mass loss of 21.4%, related to the decomposition of the organic pendant group. This corresponds to 1.22 mmol of ethylenediamine per gram of silica (Caten). The TG curve

also shows that the Caten nanomaterial is thermally stable up to 250 °C.

The FTIR spectra of SiGly and Caten (Fig. 3) exhibit the typical silica bands associated with the main inorganic framework, which has already been described in detail elsewhere [20–24]. These spectra also provide information on the progress of the reaction involving SiGly and ethylenediamine, as depicted in Fig. 1. The spectrum of SiGly displays a peak at 1254 cm<sup>-1</sup>, assigned to the epoxy ring. This peak is absent in the spectrum of Caten, thus confirming that the epoxy ring was opened during the formation of the nanocatalyst. Another important peak in the

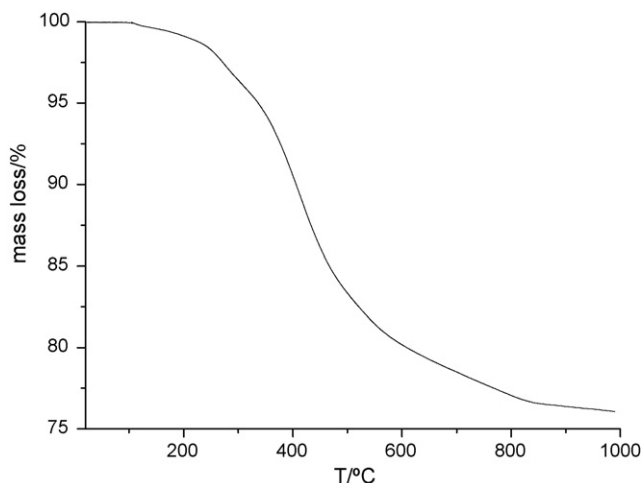


Fig. 2. Thermogravimetric curve obtained for the Caten nanocatalyst.

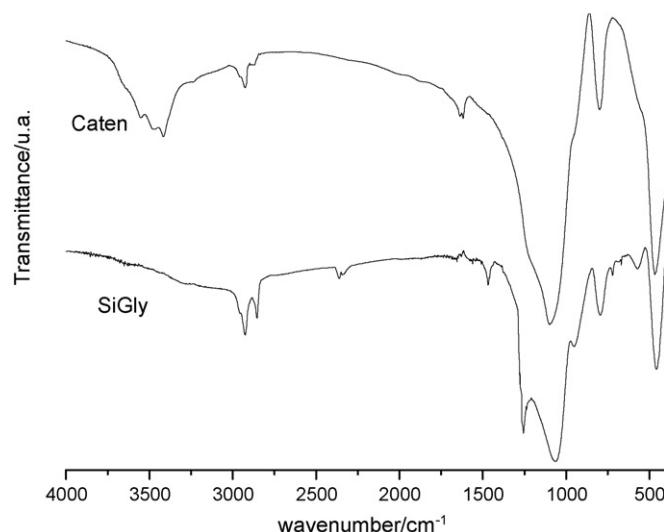


Fig. 3. Infrared spectra of SiGly and Caten.

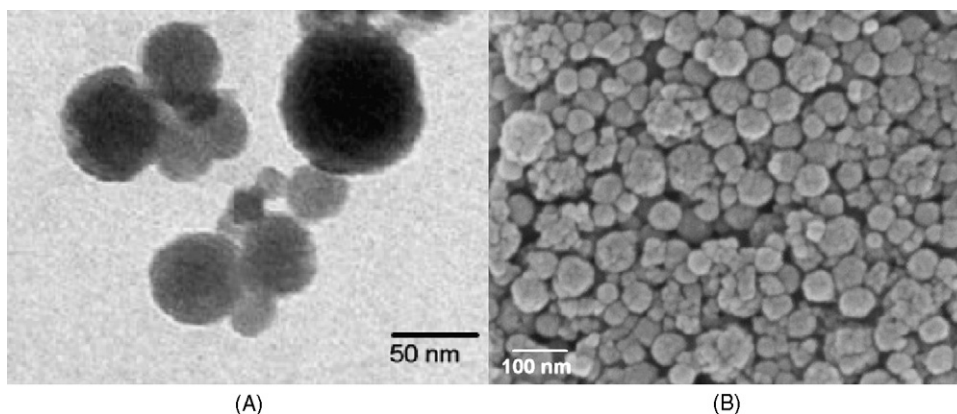


Fig. 4. TEM (A) and SEM (B) images of the Caten nanoespheres.

IR spectrum of Caten is the one related to the N–H stretching of an aliphatic amine at  $3360\text{ cm}^{-1}$ , which confirms the occurrence of the desired reaction [25].

A typical TEM image of the Caten nanocatalyst can be seen in Fig. 4A. This image reveals that the average particle size of the individual particle is about 50 nm or even smaller, and it also shows that the particles are spherical.

The SEM image of Caten (Fig. 4B) exhibits the morphology as a loose collection of small aggregates consisting of polydispersed particles smaller than 100 nm in size.

Nitrogen adsorption–desorption isotherms obtained for Caten (Fig. 5) show that the adsorption–desorption process is not reversible. This is a consequence of the hysteresis loops caused by the useful and unambiguous relation between the pressure of the capillary condensation and the pore size [26,27]. The isotherm is reversible up to a relative pressure of about 0.40. Irreversibility can be observed in the case of the samples where the condensation in primary mesopores takes place slightly above the latter pressure limit, but the adsorption and desorption branches are not parallel to each other. Instead, the

desorption curve declines abruptly for relative pressures close to 0.4–0.7, resulting in the hysteresis loop [21,26,27]. Calculation of the pore size distribution by the BJH method gave a peak around 4–6 nm, which corresponds to the steep increase in  $\text{N}_2$  adsorption around 0.4–0.7. In summary, the BET surface area of the material is  $796.10\text{ m}^2\text{ g}^{-1}$ , and the total pore volume and the BJH pore diameter calculated from the adsorption branch of the isotherm are  $0.65\text{ cm}^3\text{ g}^{-1}$  and 5.2 nm, respectively.

The solid state  $^{29}\text{Si}$  NMR spectra (Fig. 6) of both materials confirm that the covalent bond formed between the silylant agents and the silanol groups is dispersed on the silica gel surface. The spectra display four peaks, at  $-54$ ,  $-62$ ,  $-96$ , and  $-104$  ppm. The first peak is assigned to the silicon atom of the silylant agent bound to one OH group, which leads to the structure  $\text{RSi}(\text{OSi})(\text{OH})_2$ . This peak is designated the  $\text{T}^3$  signal. The peak at  $-62$  ppm can be assigned to  $\text{RSi}(\text{OSi})_3$ , the  $\text{T}^4$  signal. Both signals confirm that the organic groups are covalently linked to the silica surface. The other two peaks can be attributed to pure surface signals due to  $\text{Si}(\text{OSi})_4$  ( $\text{Q}^4$  at  $-104$  ppm) and  $\text{Si}(\text{OSi})_3\text{OH}$  ( $\text{Q}^3$  at  $-96$  ppm) [28,29].

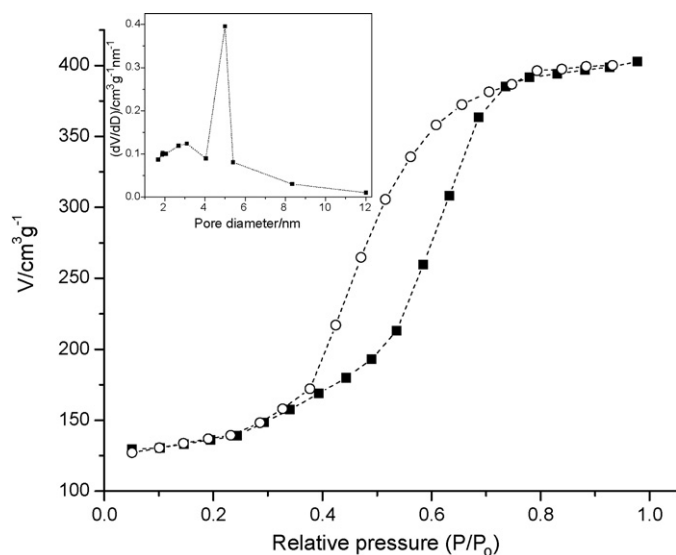


Fig. 5. Nitrogen adsorption–desorption isotherms for the Caten nanocatalyst. Insert, the corresponding BJH pore size distribution curve.

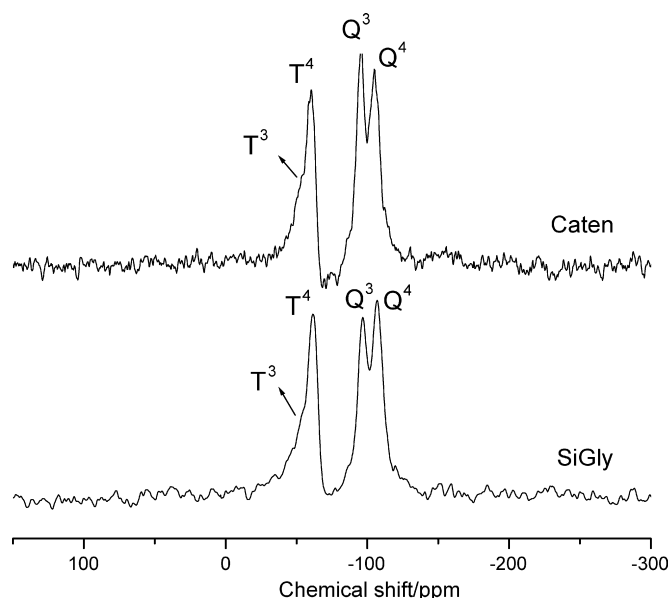


Fig. 6.  $^{29}\text{Si}$  NMR solid state spectrum of Caten and SiGly.

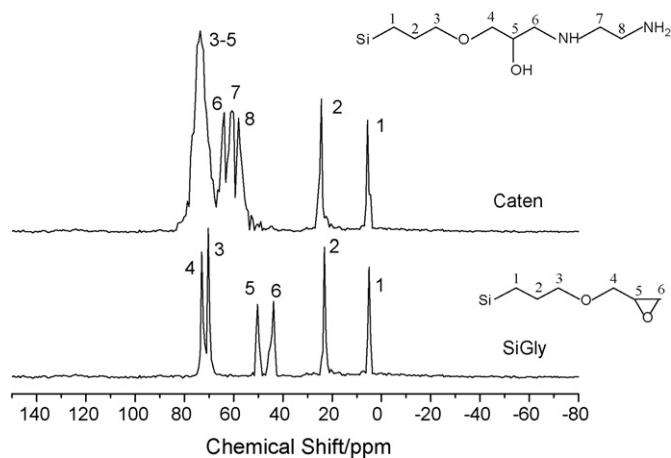


Fig. 7.  $^{13}\text{C}$  NMR solid state spectrum of Caten and SiGly.

Important information about the immobilization of the pendant groups on the inorganic structure of the catalyst was obtained by solid state  $^{13}\text{C}$  NMR, Fig. 7. The SiGly spectrum is consistent with the chemical modification of the silica surface with the glycidoxy group, since a series of signals with chemical shifts in the range of 5–73 ppm can be observed, as well as well-formed peaks at 5.0, 23.25, 43.6, 50.5, 70.2, and 73.0 ppm. These peaks can be assigned to the labeled carbons and they allow us to conclude that the glycidoxy chain units are really bound to the silicon atom. The Caten nanocatalyst spectrum gives evidence of the chemical modification of the silica surface with ethylenediamine. A series of well-formed peaks at 5.7, 24.4, 58.1, 60.7, 63.9, and 73.6 ppm helped us conclude that the ethylenediamine units are really bound to the silicon atom.

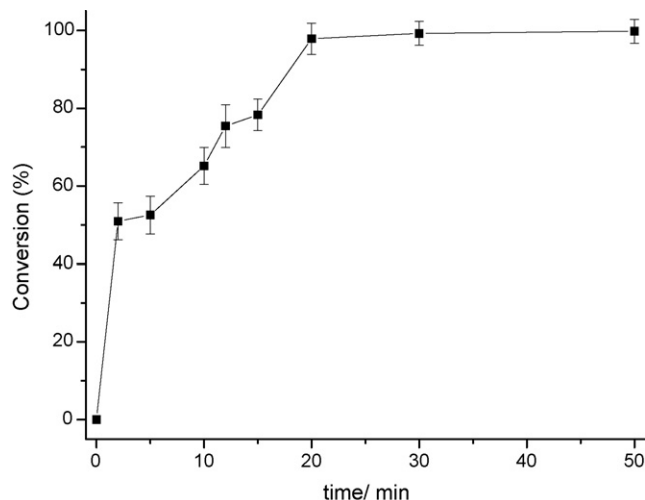


Fig. 8. Kinetic studies of 3-nitromethylcyclopentanone formation under equimolar condition, at 50 °C in EtOH.

### 3.2. Catalysis

The end of the reaction between nitromethane and cyclopentanone, which occurred after 30 min of reaction, was determined by thin layer chromatography. The product was characterized by  $^1\text{H}$  NMR spectra, which displayed a series of signals with chemical shifts in the range of 1.67–4.56 ppm: 1.67–1.78 (m, 1H); 1.97–2.07 (q, 1H); 2.19–2.30 (m, 2H); 2.30–2.47 (m, 1H); 2.50–2.59 (q, 1H); 2.93–3.10 (m, 1H) and 4.48–4.56 (d, 2H). This spectrum confirms the formation of 3-nitromethylcyclopentanone, since it is consistent with spectral data published for this compound [24–30].

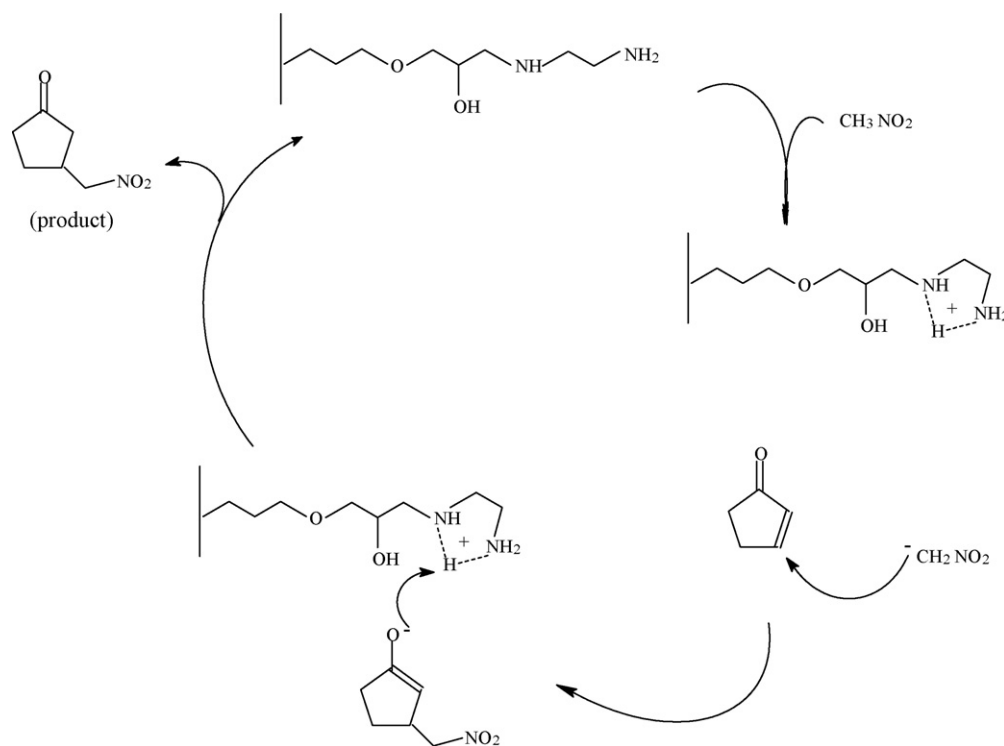


Fig. 9. Proposed catalytic cycle of Caten in the nitromethane addition to cyclopentanone.



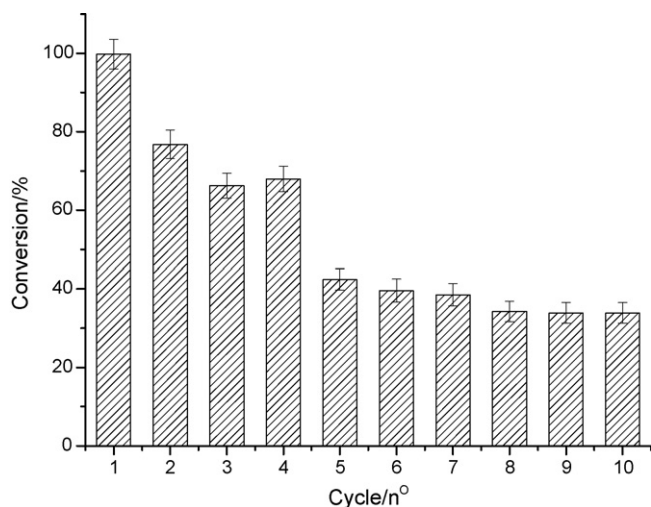


Fig. 10. Conversion yield for the recycling experiments of the Caten nanocatalyst carried out at 50 °C for 30 min.

One of the advantages of such a reaction catalyzed by the Caten nanocatalyst is the short reaction time. The kinetic studies (Fig. 8) show that the reaction reaches equilibrium at 30 min, with a product yield of 98%, under almost equimolar amounts of reactants. A similar reaction described in the literature (between cyclohexenone and nitromethane) required a much larger excess of nitromethane, a temperature of 90 °C and a reaction time of 20 h, when propylamines supported on silica were used as catalyst [31]. The catalytic cycle undergone by the Caten nanocatalyst can be explained by the mechanism proposed in Fig. 9.

In order to understand this heterogeneous catalysis, the Langmuir–Hinshelwood Eq. (1) kinetic model should be applied:

$$r_{\text{LH}} = \frac{dC}{dt} = \frac{kKC}{1 + KC} \quad (1)$$

where  $r_{\text{LH}}$  is the reaction rate,  $k$  the kinetic constant,  $K$  the Langmuir adsorption constant and  $C$  is the concentration of the formed product.

According to the Langmuir–Hinshelwood model, the number of surface adsorption sites is constant at the equilibrium, and only one substrate can bind to each surface site. Thus, the substrate adsorption rate is the same for all the sites, it does not depend on the surface coverage, and there is no interaction between the adjacent adsorbed molecules. Indeed, the addition of nitromethane to cyclopentenone depends on the adsorption of the reactants onto the Caten surface, as well as on the reaction rate.

Data obtained from Fig. 8 lead to values of  $k = 1019.47 \pm 88.21 \text{ mol L}^{-1} \text{ h}^{-1}$  and  $K = 1.06 \pm 0.08 \text{ L mmol}^{-1}$ . These results show that the adsorption involved in the catalytic process (Fig. 9) is slow, while the reaction is fast. Thus, the Langmuir–Hinshelwood model of this reaction suggests that its kinetics depends on the adsorption of the reactants on to the Caten surface.

Repeated Michael addition reactions using recycled Caten were successively performed for 10 cycles (in triplicate), under

the reaction conditions reported in Section 2. The catalyst was filtered off after each cycle, washed with ethanol, reintroduced in the system together with a new batch of nitromethane and cyclopentenone, and the reaction was repeated under conditions identical to ones used in the previous reaction. Fig. 10 shows that the catalytic activity decreases to 70% yield of 3-nitromethylcyclopentanone in cycles 2, 3, and 4. After cycle 5, the activity decreases to 40%, and it is maintained at this level up to cycle 10, when a 3-nitromethylcyclopentanone yield of 35% is obtained. This behaviour might be due to the fact that 3-nitromethylcyclopentanone is adsorbed onto the catalyst surface.

Another important aspect of this methodology is that the reactants are used in equimolar amounts. Hence, this addition is directly linked to the atom economy concept [32], which is based on the amount of starting materials and reagents incorporated into a desired product. In this way, the production of by-products or waste is minimized and the process is more atom efficient [33], which satisfies many principles of green chemistry.

#### 4. Conclusion

The methodology used here for the obtention of the solid base nanocatalyst was successful, making it a very promising synthetic route. The obtained materials exhibited homogeneous nanosize with typical basic sites. The Caten nanocatalyst proved to be very efficient for Michael addition reactions, since the product was obtained in 98% yield after only 30 min, under mild temperatures, and equimolar conditions. This nanocatalyst also presented the advantage of being easily recovered and recycled, a key principle of green chemistry. These promising results should find application in other Michael addition reactions.

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#### References

- [1] P. Claus, A. Bruckner, C. Mohr, H. Hofmeister, *J. Am. Chem. Soc.* 122 (2000) 11430.
- [2] A.I. Kozlov, A.P. Kozlova, K. Asakura, Y. Matsui, T. Kogure, T. Shido, Y. Iwasawa, *J. Catal.* 196 (2000) 56.
- [3] A. Martino, S.A. Yamanaka, J.S. Kawola, D.A. Loy, *Chem. Mater.* 9 (1997) 423.
- [4] T. Li, J. Moon, A.A. Morrone, J.J. Mecholsky, D.R. Talham, J.H. Adair, *Langmuir* 15 (1999) 4328.
- [5] U.A. Paulus, U. Endruschat, G.J. Feldmeyer, T.J. Schmidt, H. Bonnemann, R.J. Behm, *J. Catal.* 195 (2000) 383.
- [6] K. Okitsu, S. Nagaoka, S. Tanabe, H. Matsumoto, Y. Mizukoshi, Y. Nagata, *Chem. Lett.* 3 (1999) 271.
- [7] A. Yamaguchi, F. Uejo, T. Yoda, T. Uchida, Y. Tanamura, T. Yamashita, N. Teramae, *Nat. Mater.* 3 (2004) 337.
- [8] R. Ballini, F. Bigi, E. Gogni, R. Maggi, G. Sartori, *J. Catal.* 191 (2000) 348.
- [9] R. Ballini, G. Bosica, D. Livi, A. Palmieri, R. Maggi, G. Sartori, *Tetrahedron Lett.* 44 (2003) 2271.
- [10] M.L. Kantan, P. Sreekanth, *Catal. Lett.* 57 (1999) 227.

- [11] R. Ballini, G. Bosica, M.V. Gil, E. Román, J.A. Serrano, *Tetrahedron: Asymmetry* 13 (2002) 1773.
- [12] R. Ballini, D. Fiorini, M.V. Gil, A. Palmieri, *Green Chem.* 5 (2003) 475.
- [13] A. Fuerte, A. Corma, F. Sánchez, *Catal. Today* 107 (2005) 404.
- [14] R. Sercheli, R.M. Vargas, R.A. Sheldon, U. Schuchardt, *J. Mol. Catal. A* 148 (1999) 173.
- [15] R. Ballini, G. Bosica, D. Fiorini, A. Palmieri, M. Petrini, *Chem. Rev.* 105 (2005) 933.
- [16] I. Ledneczki, M. Darányi, F. Fülöp, A. Molnar, *Catal. Today* 100 (2005) 437.
- [17] H. Firouzabadi, N. Iranpoor, M. Jafarpour, A. Ghaderi, *J. Mol. Catal. A* 252 (2006) 150.
- [18] X. Wang, S. Cheng, *Catal. Commun.* 7 (2006) 689.
- [19] H. Firouzabadi, N. Iranpoor, M. Jafarpour, A. Ghaderi, *J. Mol. Catal. A* 249 (2006) 98.
- [20] A.G.S. Prado, E. DeOliveira, *J. Colloid Interf. Sci.* 291 (2005) 53.
- [21] A.G.S. Prado, C. Airoidi, *J. Mater. Chem.* 12 (2002) 3823.
- [22] P.T. Tanev, T.J. Pinnavaia, *Chem. Mater.* 8 (1996) 2068.
- [23] D.J. Macquarrie, *Phil. Trans. R. Lond. A* 358 (2000) 419.
- [24] E. DeOliveira, J.D. Torres, C.C. Silva, A.A.M. Luz, P. Bakuzis, A.G.S. Prado, *J. Braz. Chem. Soc.* 17 (2006) 994.
- [25] J.A.A. Sales, A.G.S. Prado, C. Airoidi, *Polyhedron* 21 (2002) 2647.
- [26] O. Franke, G. Schulz-Ekloff, J. Rathousky, J. Starek, A. Zukal, *J. Chem. Soc., Chem. Commun.* (1993) 724.
- [27] P.J. Branton, P.G. Hall, K.S.W. Sing, *J. Chem. Soc., Chem. Commun.* (1993) 1257.
- [28] X.H. Zhang, N. Zhao, W. Wei, Y. Sun, *Catal. Today* 115 (2006) 102.
- [29] J.A.A. Sales, A.G.S. Prado, C. Airoidi, *Surf. Sci.* 590 (2005) 51.
- [30] S. Hanessian, P. Pham, *Org. Lett.* 2 (2000) 2975.
- [31] D.J. Macquarrie, R. Maggi, A. Mazzacani, G. Sartori, R. Sartorio, *Appl. Catal. A* 246 (2003) 183.
- [32] B.M. Trost, *Science* 254 (1991) 1471.
- [33] A.G.S. Prado, *Quim. Nova* 26 (2003) 738.